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<p>(54) Title: HYDROPHOBICALLY MODIFIED ANIONIC CELLULOSE ETHERS</p> <p>(57) Abstract</p> <p>The invention relates to a hydrophobically modified anionic cellulose ether obtainable by a process comprising reacting an alkali metal cellulose with at least three alkylating reagents A, B, and C. Reagent A is selected from the group of haloacetic acids, alkali metal haloacetates, alkali metal vinyl sulfonates, and vinyl sulfonic acid. Reagent B has the formula <math>R^1-(OCH_2CH(R^2))_n-P</math>, wherein <math>R^1</math> represents a <math>C_2-C_7</math> group, <math>R^2</math> is hydrogen or a methyl group, <math>n</math> is 0-2, and <math>P</math> represents a glycidyl ether group, a 3-halo-2-hydroxypropyl ether group, a 1,2-epoxy group, or a halide, and reagent C has the formula <math>R^3-(OCH_2CH(R^2))_m-P</math>, wherein <math>R^3</math> represents a <math>C_8-C_{30}</math> group, <math>m</math> is 0-10, and <math>R^2</math> and <math>P</math> have the meaning as described above.</p>		

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## HYDROPHOBICALLY MODIFIED ANIONIC CELLULOSE ETHERS

- 5 The invention relates to a hydrophobically modified anionic cellulose ether, such as hydrophobically modified carboxymethyl cellulose.

Processes for preparing polysaccharides, such as cellulose, starch, and guar, having hydrophobic substituents are known in the art. For instance,  
10 EP-A-0384167 describes a slurry process, using a diluent system, for preparing water-soluble polysaccharides, in particular hydroxyethyl cellulose (HEC) derivatives, containing alkylaryl substituents having at least about 10 carbon atoms, for use in latex compositions.

The process comprises reacting an ether-substituted polysaccharide with  
15 an alkylaryl hydrophobe-containing compound. It is mentioned that as a result of reacting a polysaccharide ether with an alkylaryl hydrophobe, the ether substitution on the polysaccharide provides an increase in hydrophobic substitution as compared with the unsubstituted saccharide.

Examples 35 and 36 of EP-A-0384167 show that when using nonylphenyl  
20 glycidyl ether a higher alkylarylation efficiency is observed with polysaccharides having a higher ethylene oxide (as hydroxyethyl) molar substitution (MS) value. MS is defined as the average moles of a substituent per mole of sugar repeating unit. With an ethylene oxide MS of 3.5 a hydrophobe MS of 0.059 with an efficiency of 24% was obtained,  
25 while with an ethylene oxide MS of 2.3 a hydrophobe MS of 0.025 with an efficiency of 10% was observed. The obtained hydrophobic substitution efficiency therefore is low.

Thus, a disadvantage of this process is that the hydrophobic substitution  
30 proceeds with a low efficiency, resulting in a waste of chemicals and a burden on the environment. A further drawback is that the efficiency with

which hydrophobic groups are incorporated is dependent on the presence of hydroxyethyl groups per se and only increases with an increasing number of such groups. This is due to the fact that the hydroxyalkyl substituents are more prone to alkylation than the hydroxyl groups on the  
5 sugar repeating unit.

Processes for preparing hydrophobically derivatized polysaccharides are also known from EP-A-0566911 and EP-A-0307915. The process of EP-A-0566911 comprises reacting a polysaccharide with an alkyl halide, an  
10 alkylene oxide, or a chloroacetic acid in the presence of an alkali, reacting the modified polysaccharide with a hydrophobic alkyl or alkylaryl reagent having 8 to 24 carbon atoms and containing a nucleophilic reactive group selected from a glycidyl ether and an isocyanate, to produce a water-soluble, hydrophobically modified polysaccharide. This hydrophobically  
15 modified polysaccharide is subsequently depolymerized by reaction with hydrogen peroxide to the desired level. The following polysaccharides have been hydrophobically modified: poly(vinyl alcohol), carboxymethyl hydroxypropyl starch, methyl hydroxyethyl cellulose, methyl hydroxypropyl cellulose, hydroxypropyl guar, carboxymethyl hydroxyethyl cellulose, and  
20 HEC.

EP-A-0566911 describes, *int. al.*, a slurry process in which use was made of stearyl isocyanate and nonylphenyl glycidyl ether. HEC was modified using hexadecyl glycidyl ether, and the weight percentage of hydrophobe in the (depolymerized) product was from 0.4 to 1.4% (Example 1). This  
25 corresponds to a low hydrophobe MS of approximately 0.005 and 0.02, respectively. A similarly low hydrophobe MS of approximately 0.01 was calculated for carboxymethyl hydroxyethyl cellulose (CMHEC) derivatized with hexadecyl glycidyl ether (Table 4, No. 13). Hydrophobic substitution

efficiencies could not be calculated on the basis of information given in this publication, but these are estimated to be low as well.

EP-A-0307915 describes a process for preparing water-soluble hydrophobic CMHEC modified with an alkyl,  $\alpha$ -hydroxyalkyl, or acyl group  
5 having 8 to 25 carbon atoms. In the Preparation Example the hexadecyl hydrophobe only represents 0.7 percent by weight of the cellulose. A hydrophobic substitution efficiency of 6.7% was calculated. The slurry process preferably is carried out by first hydroxyethylating the cellulose, then attaching the hydrophobe, and finally carboxymethylating the product.  
10 The processes of EP-A-0566911 and EP-A-0307915 have the same disadvantages as mentioned above for EP-A-0384167, i.e., a low hydrophobic substitution efficiency and the incorporation of hydroxyethyl groups. In particular, these publications do not disclose a process for preparing hydrophobically modified anionic cellulose ethers, e.g.  
15 hydrophobically modified carboxymethyl cellulose (CMC), not carrying a hydroxyalkyl group.

Several other processes have been described in the art, in particular relating to the preparation of hydrophobically modified non-ionic cellulose  
20 ethers, i.e. US 4228277, US 4243802, EP-A-0390240, US 5120838, US 5124445, EP-A-0362769, EP-A-0471866, and US 5504123.

In US 5566760 a process is described for the preparation of hydrophobically modified guar derivatives.  
25

Finally, EP-A-0189935 describes water-soluble, hydrophobically derivatized, quaternary nitrogen-containing polysaccharides, in particular derived from HEC. Only quaternary ammonium cellulose derivatives are disclosed. HEC is hydrophobically modified by alkylation with a quaternary

nitrogen-containing compound, such as 3-chloro-2-hydroxypropyl trimethyl ammonium chloride, and an alkylhalide hydrophobe, for example dodecyl bromide. In Run 35, a low hydrophobe MS of 0.016 was obtained. A hydrophobic substitution efficiency of 13% was calculated. However, it is  
5 not always desirable to incorporate a quaternary ammonium group into a hydrophobically modified polysaccharide.

The above-mentioned prior art does not disclose hydrophobically modified anionic cellulose ethers, in particular hydrophobically modified CMC, not  
10 carrying a hydroxyalkyl group. The present invention provides such ethers and an economical process for preparing them.

The hydrophobically modified anionic cellulose ether according to the present invention is obtainable by a process comprising reacting an alkali  
15 metal cellulose with at least three alkylating reagents A, B, and C,

-one or more reagents A being selected from the group of haloacetic acids, alkali metal haloacetates, alkali metal vinyl sulfonates, and vinyl sulfonic acid,  
20

-one or more reagents B having the formula



wherein  $R^1$  represents a  $C_2$ - $C_7$  group,  $R^2$  is hydrogen or a methyl group,  $n$  is 0-2, and  $P$  represents a glycidyl ether group, a 3-halo-2-hydroxypropyl  
25 ether group, a 1,2-epoxy group, or a halide, and

-one or more reagents C having the formula



wherein  $R^3$  represents a  $C_8$ - $C_{30}$  group,  $m$  is 0-10, and  $R^2$  and  $P$  have the meaning as described above.

5 The hydrophobically modified anionic cellulose ethers according to the present invention can be prepared from readily available cellulose starting materials. These materials include cotton linters and purified high-alpha wood pulp.

10 Typically, the cellulose is reacted with an aqueous solution of an alkali metal hydroxide to prepare the alkali metal cellulose. Suitable alkali metal hydroxides include sodium hydroxide, potassium hydroxide, and lithium hydroxide, with sodium hydroxide being preferred.

15 Suitable reagents A for the process of the present invention include chloroacetic acid, sodium chloroacetate, and sodium vinyl sulfonate. A mixture of, for example, chloroacetic acid and sodium vinyl sulfonate may also be used, and this results in the preparation of a hydrophobically modified carboxymethyl sulfoethyl cellulose. It is preferred that reagent A consists essentially of chloroacetic acid.

20 Suitable reagents B include benzyl chloride, allyl chloride, chloroethyl butyl ether, ethyl glycidyl ether, butyl glycidyl ether, butoxyethyl glycidyl ether, tert-butyl glycidyl ether, iso-butyl glycidyl ether, allyl glycidyl ether, propyl glycidyl ether, isopropyl glycidyl ether, benzyl glycidyl ether, and benzyl  
25 halides. Preferably,  $P$  is a glycidyl ether group. It is also preferred that  $R^2$  is hydrogen. Further, it is preferred that  $n$  equals 0. Preferred alkylating reagents B are butyl glycidyl ether and benzyl chloride.



Reagent C contains the hydrophobic group. The group  $R^3$  preferably has 8 to 22, more preferably 12 to 22, carbon atoms. Reagents C suitable for the invention process include compounds wherein  $R^3$  represents a nonylphenyl, 2-ethylhexyl, dodecyl, tetradecyl, hexadecyl, octadecyl or hexacosyl group.  $R^3$  may be derived from (naturally occurring) fatty acids such as coconut, tallow, and hydrogenated tallow fatty acid. Reagent C may optionally contain one or more oxygen atoms in the form of ethyloxy or propyloxy groups. Typical examples thereof are tetradecyl-penta-oxyethyl glycidyl ether, hexadecyl-bis-oxyethyl glycidyl ether, and octadecyl-bis-oxyethyl glycidyl ether. Preferred alkylating reagents C are dodecyl glycidyl ether, tetradecyl glycidyl ether, hexadecyl glycidyl ether, octadecyl glycidyl ether, dodecyl-bis-oxyethyl glycidyl ether, tetradecyl-bis-oxyethyl glycidyl ether, hexadecyl-bis-oxyethyl glycidyl ether, octadecyl-bis-oxyethyl glycidyl ether, tetradecyl-penta-oxyethyl glycidyl ether, and mixtures thereof.

15 Preferably,  $m$  is 0-5 and  $R^2$  is hydrogen. It is to be noted that for  $n=1-2$  and  $m=1-10$   $n$  and  $m$  are average numbers.

The process of the present invention may be conducted at any desired reaction temperature, typically between 20 and 125°C and preferably from about 55 to 105°C, for a sufficient time to provide the desired level of hydrophobic substitution, typically from about 1 to 24 hours or more. The reaction may be conducted in a relatively large amount of diluent or with a minimal amount of diluent as desired, i.e., using either a so-called slurry or a so-called dry process.

25 In this specification, the term slurry process means a process wherein the weight ratio of liquid medium to cellulose is greater than 10, while a dry process means a process wherein the weight ratio of liquid medium to cellulose is equal to or smaller than 10, preferably smaller than 5, more



preferably smaller than 3. Typically, a dry process is carried out in a high-efficiency intensive mixer, e.g. a plowshare mixer.

Suitable diluents include ethanol, isopropyl alcohol, tert-butyl alcohol, acetone, water, methyl ethyl ketone, and mixtures thereof.

5

The reaction can be carried out in any reaction vessel or reactor. The vessel or reactor is suitably equipped with a stirrer or mixing gear, a nitrogen inlet tube, a condenser, and facilities for heating. A particularly suitable reactor is a Drais<sup>®</sup> or a Lödige<sup>®</sup> reactor.

10

The molar ratio of alkali metal hydroxide per sugar repeating unit may vary depending on the alkylating agents used. Typically, a molar ratio of between 0.001 and 5 is used. Depending on the nature of the alkylating reagent(s) used, additional alkali metal hydroxide is added. For instance, when using chlorinated alkylating agents, e.g. chloroacetic acid, an additional molar equivalent of hydroxide is required. When using a glycidyl ether a catalytic amount of alkali metal hydroxide is sufficient.

15

Many polysaccharides when in contact with any base are readily degraded by oxygen. Accordingly, it is preferred to exclude oxygen from the reaction vessel during the time the alkali metal hydroxide is present. The reaction is suitably carried out in an atmosphere of an inert gas, preferably nitrogen.

20

After the reaction of the cellulose with a suitable amount of an aqueous solution of an alkali metal hydroxide, the alkali metal cellulose may be reacted first with alkylating reagent A, followed by a reaction with alkylating reagent B, and then C, or with a mixture of B and C, at a suitable temperature and for a time sufficient to provide the desired level of hydrophobic substitution. Alternatively, alkylating reagent B followed by C, or a mixture of B and C, may be added first, after which alkylating reagent

25

A is allowed to react, or the alkali metal cellulose may be simultaneously reacted with alkylating reagents A, B, and C. It was found that if the alkali metal cellulose is reacted first with a mixture of B and C, and then with A, the first reaction step can be carried out in the presence of only water. A  
5 further alternative reaction path is to first add a small amount of reagent A, then reagents B and C, either sequentially or simultaneously, and finally the remainder of reagent A.

A preferred embodiment of the invention process is the reaction of the alkali metal cellulose first with a mixture of alkylating reagents B and C and  
10 then with reagent A, in particular when using chloroacetic acid.

It is preferred to carry out the process of the invention by means of the so-called dry process using a minimal amount of a suitable diluent, in particular water, that is, just enough to allow the polysaccharide to swell  
15 while preventing dissolution. The cellulose, in the form of fibres, linters or a powder, is allowed to react with an aqueous solution of an alkali metal hydroxide, i.e. the so-called alkalization, and the obtained alkali metal cellulose is reacted with reagents A, B, and C as described above, with the temperature gradually being increased from about 10 to about 105°C. The  
20 reagents can be added pure or as a solution in a suitable diluent, e.g., a solution of chloroacetic acid in ethanol can suitably be used.

A particularly preferred process according to the invention comprises a dry process in which reagent B followed by C, or a mixture of B and C, is reacted with the alkali metal cellulose in the presence of water, prior to  
25 reaction with reagent A. Typically, the amount of water present during alkylation is between 2 and 12 moles per mole cellulose. Preferably, an amount of 3.5-10 moles/mole cellulose is used. The reaction with reagent A preferably is carried out in an aqueous alcohol medium, in particular it is

performed in the presence of isopropanol or ethanol, with the water stemming from the alkalization.

A person skilled in the art will readily be able to select suitable molar ratios  
5 of the reactants per sugar repeating unit for the invention process. For reagent A a molar ratio of between 0.3 and 3.5 is suitable. A ratio of between 0.5 and 2.5 is preferred. For reagent B a molar ratio of between 0.02 and 1.5 is suitable, a ratio of between 0.05 and 1 being preferred. For reagent C a molar ratio of between 0.001 and 1 is suitable, preferably a  
10 ratio of between 0.005 and 0.5.

In another embodiment of the process of the present invention, a fourth alkylating reagent, i.e., a quaternary ammonium compound D, is used. Hydrophobically modified quaternary ammonium-containing poly-  
15 saccharides are known in the art, e.g., from EP-A-0189935.

Typically, compound D is a 3-trialkylammonium-1,2-epoxypropane halide wherein each of the alkyl groups is a methyl, ethyl, benzyl, or long-chain alkyl group. Preferably, 3-trimethylammonium-1,2-epoxypropane chloride or 1-chloro-2-hydroxy-3-trimethylammoniumpropane chloride is used.

20

The hydrophobically modified celluloses of the present invention may be used in, for example, anti-settling, associative thickening, and in foam, emulsion, and suspension stabilizations. These celluloses are important for various industries including the drilling industry and paints, for example,  
25 latex compositions; cosmetics, such as shampoos; biomedicine, such as in oral care including toothpaste or in pharmaceuticals including timed-release formulations or controlled-release formulations; detergents, such as in laundry or surface cleaners; soil release; various other timed-release

applications including pesticides; and other areas in which a protective colloid, stabilizer, emulsifier, thickener, or rheology modifier is desired.

The process defined in claim 1 can also be used for the preparation of  
5 anionic hydrophobically modified polysaccharide ethers derived from hydroxyethyl cellulose, ethyl hydroxyethyl cellulose, guar, and starch.

Using a combination of reagents B and C as described herein, non-ionic hydrophobically modified cellulose, hydroxyethyl cellulose, ethyl hydroxyethyl cellulose, guar, and starch can be prepared.

10

The invention is illustrated by the following examples.

#### EXPERIMENTAL

##### Materials:

- 15 Linters Cellulose (0.5 mm milled), ex Buckeye  
n-Butyl glycidyl ether, 95%, ex CFZ  
Dodecyl/tetradecyl glycidyl ether, tech., ex Aldrich  
Nafol®1214-2EO glycidyl ether: a mixture of dodecyl-bis-oxyethyl glycidyl ether and tetradecyl-bis-oxyethyl glycidyl ether, 85%
- 20 Nafol®1214, ex Condea  
Isopropyl alcohol, 99.5%, ex Fluka  
Ethanol, 95%, ex Baker  
Sodium hydroxide, 50% in water, ex Acros  
Chloroacetic acid, 99%, ex Akzo Nobel
- 25 Acetic acid, 99.8%, ex Baker  
Benzyl chloride, 99%, ex Fluka

Nafol®1214-2EO glycidyl ether was prepared according to the method described in EP-A-0390240 in Example A starting from a mixture of 1-

dodecanol and 1-tetradecanol, i.e. Nafol®1214. Following the same method, tetradecyl-penta-oxyethyl glycidyl ether, a mixture of hexadecyl- and octadecyl-bis-oxyethyl glycidyl ether, and a mixture of dodecyl- and tetradecyl-bis-oxyethyl glycidyl ether were prepared from the corresponding  
5 (mixture of) alcohols.

The reactions were carried out in a Drais® Turbulent Mixer, type TR2.5, reactor. The knife blades were stirred at 180 rpm. The reactor was heated by a Thermomix UB water/oil bath.

10

The epoxide conversions were determined by titration using a Methrom 614 Impulsomat in combination with a Methrom 625 dosigraph or a Metrohm E536 potentiograph. The MS and DS values were determined using a 300 MHz Bruker NMR spectrometer, as specified by F. Cheng et al. in Journal  
15 of Applied Polymer Science, Vol. 61, 1831-1838 (1996). CM stands for carboxymethyl, BGE for n-butyl glycidyl ether, BEGE for butyloxyethyl glycidyl ether, and FAE for fatty (ethoxylated) alkyl ether. The efficiency of introducing the alkylating group into the polysaccharide is given as a percentage in parentheses behind the DS and MS values. The viscosities  
20 of a 1% solution of products were measured at room temperature and 30 rpm with a Brookfield LVT viscometer.

#### COMPARATIVE EXAMPLE A

About 50% of a solution of sodium hydroxide (80.8 g, 2.02 moles) in water  
25 (120 ml) was added to a stirred mixture of Linters Cellulose (150 g), 40 ml of water, and Nafol®1214-2EO glycidyl ether (120 g, 0.3 mole) under a nitrogen atmosphere at 20°C. After 1 hour the mixture was heated at 85°C for 25 hours. The mixture was cooled, and 450 ml of ethanol, the remaining 50% of the sodium hydroxide solution, and a solution of chloroacetic acid

(76.5 g, 0.8 mole) in 20 ml of ethanol were added. The mixture was heated at 80°C for 90 minutes, cooled, and neutralized with acetic acid (24 g, 0.4 mole). The crude product was washed three times each with 65% ethanol, 80% ethanol, ethanol, and acetone, and was dried under reduced pressure at 70°C for 24 hours. A white powder was obtained with the following analysis:  $DS_{CM}$  0.75 (83%),  $MS_{FAE}$  0.02 (6%), and a viscosity of 360 mPa.s (fair solubility in water).

#### EXAMPLE 1

About 30% of a solution of sodium hydroxide (80.8 g, 2.02 moles) in water (120 ml) was added to a stirred mixture of Linters Cellulose (150 g), 40 ml of water, n-butyl glycidyl ether (60 g, 0.4 mole), and Nafol®1214-2EO glycidyl ether (90 g, 0.22 mole) under a nitrogen atmosphere at 20°C. After 1 hour the mixture was heated at 85°C for 25 hours. The mixture was cooled and 450 ml of ethanol, the remaining 70% of the sodium hydroxide solution, and a solution of chloroacetic acid (76.5 g, 0.8 mole) in 20 ml of water were added. The mixture was heated at 80°C for 90 minutes, cooled, and neutralized with acetic acid (24 g, 0.4 mole). The crude product was washed three times each with 65% ethanol, 80% ethanol, ethanol, and acetone, and was dried under reduced pressure at 70°C for 24 hours. A white powder was obtained with the following analysis:  $DS_{CM}$  0.75 (83%),  $MS_{BGE}$  0.23 (51%), and  $MS_{FAE}$  0.09 (36%). The product swells but is insoluble in water.

#### 25 COMPARATIVE EXAMPLE B

A solution of sodium hydroxide (80.8 g, 2.02 moles) in 120 ml of water was added to a stirred mixture of Linters Cellulose (150 g) and 40 ml of water under a nitrogen atmosphere at 20°C. A solution of chloroacetic acid (75.6 g, 0.8 mole) in water (20 ml) and Nafol®1214-2EO glycidyl ether (120 g, 0.3

mole) were added after 17 hours. The mixture was heated at 85°C for 26 hours. The mixture was cooled and neutralized with 24 g (0.4 mole) acetic acid. The crude product was washed three times each with 65% ethanol, 80% ethanol, ethanol, and acetone, and was dried under reduced pressure at 70°C for 24 hours. A white powder was obtained with the following analysis:  $DS_{CM}$  0.64 (71%),  $MS_{FAE}$  0 (0%), and a viscosity of 5800 mPa.s.

## EXAMPLE 2

A solution of sodium hydroxide (80.8 g, 2.02 moles) in 120 ml of water was added to a stirred mixture of Linters Cellulose (150 g) and 40 ml of water under a nitrogen atmosphere at 20°C. A solution of chloroacetic acid (75.6 g, 0.8 mole) in water (20 ml), n-butyl glycidyl ether (60 g, 0.4 mole), and Nafol®1214-2EO glycidyl ether (90 g, 0.22 mole) were added after 17 hours. The mixture was heated at 85°C for 26 hours. The mixture was cooled and neutralized with 24 g (0.4 mole) acetic acid. The crude product was washed three times each with 65% ethanol, 80% ethanol, ethanol, and acetone, and was dried under reduced pressure at 70°C for 24 hours. A white powder was obtained with the following analysis:  $DS_{CM}$  0.65 (72%),  $MS_{BGE}$  0.21 (47%),  $MS_{FAE}$  0.07 (28%), and a viscosity of 780 mPa.s.

## EXAMPLE 3

A solution of sodium hydroxide (40 g, 1.0 mole) in 60 ml of water was added to a stirred mixture of Linters Cellulose (150 g), 40 ml of water, and n-butyl glycidyl ether (60 g, 0.4 mole) under a nitrogen atmosphere at 20°C. After 30 minutes the mixture was heated at 100°C for 5 hours. The mixture was cooled and neutralized with acetic acid (60 g, 1.0 mole). The crude product was washed three times each with 65% ethanol, 80% ethanol, ethanol, and acetone, and was dried under reduced pressure at 70°C for



24 hours. A white powder, i.e., BGEC, was obtained with the following analysis:  $MS_{BGE}$  0.23 (51%).

A solution of sodium hydroxide (40 g, 1.0 mole) in 60 ml of water was added to a stirred mixture of BGEC (154 g, 0.8 mole), 40 ml of water, and  
5 Nafol®1214-2EO glycidyl ether (80 g, 0.2 mole) under a nitrogen atmosphere at 20°C. After 30 minutes the mixture was heated at 100°C for 5 hours. The mixture was cooled and neutralized with acetic acid (60 g, 1.0 mole). The crude product was washed three times each with 65% ethanol, 80% ethanol, ethanol, and acetone, and was dried under reduced pressure  
10 at 70°C for 24 hours. A white powder, i.e., BGE/FAEC, was obtained with the following analysis:  $MS_{BGE}$  0.23 (51%) and  $MS_{FAE}$  0.14 (56%). This product subsequently was carboxymethylated using a three-necked roundbottom flask instead of the Drais mixer.

A solution of sodium hydroxide (17.2 g, 0.43 mole) in 26 ml of water was  
15 added to a stirred mixture of BGE/FAEC (26.4 g, 0.11 mole) in 1 l of isopropyl alcohol and 50 ml of water under a nitrogen atmosphere at 20°C. After 90 minutes a solution of chloroacetic acid (15.6 g, 0.165 mole) in 20 ml of isopropyl alcohol was added. The mixture was heated at 65°C for 1 hour and at 80°C for 2 hours, cooled and neutralized with acetic acid (6 g,  
20 0.1 mole). The crude product was washed three times each with 65% ethanol, 80% ethanol, ethanol, and acetone and was dried under reduced pressure at 70°C for 24 hours. A white powder was obtained with the following analysis:  $DS_{CM}$  0.99 (66%),  $MS_{BGE}$  0.23 (51%), and  $MS_{FAE}$  0.14 (56%). The product swells but is insoluble in water.

25

#### EXAMPLE 4

A solution of sodium hydroxide (28 g, 0.7 mole) in 28 ml of water was added to a stirred mixture of carboxymethyl cellulose (179 g) with a degree of carboxymethyl substitution of 0.19, n-butyl glycidyl ether (41.9 g, 0.3

mole), tetradecyl-penta-oxyethyl glycidyl ether (61.3 g, 0.1 mole), and 103 ml of water under a nitrogen atmosphere at 20°C. After 1 hour the mixture was heated at 100°C for 5 hours. The mixture was then cooled and taken up in 2 l of 65% aqueous ethanol and neutralized with acetic acid. The  
5 crude product was filtered and washed with 65% ethanol, 80% ethanol, 80% acetone, and acetone, and dried under reduced pressure at 90°C for 24 hours. An off-white powder was obtained with the following analysis:  $DS_{CM}$  0.19,  $MS_{BGE}$  0.19 (63%),  $MS_{FAE}$  0.039 (39%).

#### 10 COMPARATIVE EXAMPLE C

A solution of sodium hydroxide (52 g, 1.3 moles) in 52 ml of water was added to a stirred mixture of cellulose (168 g), tetradecyl-penta-oxyethyl glycidyl ether (122.6 g, 0.2 mole) and 75 ml of water under a nitrogen atmosphere at 20°C. After 45 minutes the mixture was heated at 100°C for  
15 4 hours. The mixture was cooled and taken up in 2 l of 65% aqueous ethanol and neutralized with acetic acid. The crude product was filtered and washed with 65% ethanol, water, 80% ethanol, ethanol, and acetone, and dried in a fluid bed dryer. An off-white powder was obtained with the following analysis:  $MS_{FAE}$  0.01 (5%).

20

#### EXAMPLE 5

A solution of sodium hydroxide (52 g, 1.3 moles) in 52 ml of water was added to a stirred mixture of cellulose (168 g), 2-butoxyethyl glycidyl ether (BEGE) (58.6 g, 0.3 mole) tetradecyl-penta-oxyethyl glycidyl ether (61.3 g,  
25 0.1 mole) and 75 ml of water under a nitrogen atmosphere at 20°C. After 90 minutes the mixture was heated at 100°C for 4 hours. The mixture was cooled and taken up in 2 l of 65% aqueous ethanol and neutralized with acetic acid. The crude product was filtered and washed with 65% ethanol, water, 80% ethanol, ethanol, and acetone, and dried under reduced

pressure at 70°C. An off-white powder was obtained with the following analysis:  $MS_{\text{BEGE}}$  0.14 (47%),  $MS_{\text{FAE}}$  0.025 (25%).

This product was subsequently carboxymethylated using the procedure described in Example 3.

5

#### EXAMPLE 6

##### *Preparation of benzyl carboxymethyl cellulose*

A solution of sodium hydroxide (148 g, 3.7 moles) in 148 ml of water was added to a stirred mixture of linters cellulose (205 g) and benzyl chloride  
10 (467 g, 3.7 moles) under a nitrogen atmosphere at 20°C. A solution of chloroacetic acid (116.6 g, 1.23 moles) in 30 ml of water was added after 4 hours. The mixture was heated at 90°C for 5 hours. The mixture was cooled and taken up in 2.5 l of 65% aqueous ethanol and neutralized with acetic acid. The crude product was filtered and washed with 65% ethanol,  
15 80% ethanol, ethanol, and acetone, and dried in a fluid bed dryer at 70°C. A white powder was obtained.

##### *Preparation of hydrophobically modified benzyl carboxymethyl cellulose*

A solution of sodium hydroxide (32 g, 0.8 mole) in 48 ml of water was  
20 added to a stirred mixture of benzyl carboxymethyl cellulose (200 g) and a mixture of dodecyl and tetradecyl-bis-oxyethyl glycidyl ether (61.6 g 0.15 mole) under a nitrogen atmosphere at 20°C. After 60 minutes the mixture was heated at 100°C for 4 hours. The mixture was cooled and neutralized with acetic acid. The crude product was taken up in 2 l of 65% aqueous  
25 ethanol, filtered, and washed with 65% ethanol, 80% ethanol, and acetone, and dried under reduced pressure at 70°C. A white powder was obtained.

## EXAMPLE 7

About 38% of a solution of sodium hydroxide (104 g, 2.6 moles) in 156 ml of water was added to a stirred mixture of cellulose (150 g), n-butyl glycidyl ether (30 g, 0.22 mole), a mixture of dodecyl and tetradecyl glycidyl ether (40 g, 0.15 mole), and 50 ml of water under a nitrogen atmosphere at 20°C. After 60 minutes the mixture was heated at 100°C for 4 hours. The mixture was cooled and 250 ml of ethanol, the remaining 62% of the sodium hydroxide solution, and a solution of chloroacetic acid (104 g, 1.1 moles) in 25 ml of water were added. The mixture was heated at 80°C for 2 hours, cooled, and neutralized with acetic acid (24 g, 0.4 mole). The crude product was washed three times each with 65% ethanol, 80% ethanol, ethanol, and acetone, and was dried under reduced pressure at 70°C. A white powder was obtained with the following analysis:  $DS_{CM}$  0.84 (69%),  $MS_{BGE}$  0.09 (37%),  $MS_{FAE}$  0.019 (11%).

15

## EXAMPLE 8

About 33% of a solution of sodium hydroxide (104 g, 2.6 moles) in 156 ml of water was added to a stirred mixture of cellulose (150 g), n-butyl glycidyl ether (30 g, 0.22 mole), and 50 ml of water under a nitrogen atmosphere at 20°C. After 60 minutes the mixture was heated at 100°C for 1 hour. A mixture of hexadecyl- and octadecyl-bis-oxyethyl glycidyl ether (30 g, 0.06 mole) was added to the hot reaction mixture and heated at 100°C for another 4 hours. The mixture was cooled and 250 ml of ethanol, the remaining 67% of the sodium hydroxide solution, and a solution of chloroacetic acid (104 g, 1.1 moles) in 25 ml of water were added. The mixture was heated at 80°C for 2 hours, cooled, and neutralized with acetic acid (24 g, 0.4 mole). The crude product was washed three times each with 65% ethanol, 80% ethanol, ethanol, and acetone, and was dried under reduced pressure at 70°C. A white powder was obtained with the following

25

analysis:  $DS_{CM}$  0.87 (71%),  $MS_{BGE}$  0.043 (27%),  $MS_{FAE}$  0.012 (18%) and a viscosity of 416 mPa.s.

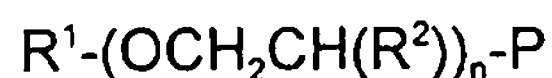
## CLAIMS

1. A hydrophobically modified anionic cellulose ether obtainable by a process comprising reacting an alkali metal cellulose with at least three  
5 alkylating reagents A, B, and C,

-one or more reagents A being selected from the group of haloacetic acids, alkali metal haloacetates, alkali metal vinyl sulfonates, and vinyl sulfonic acid,

10

-one or more reagents B having the formula



wherein  $R^1$  represents a  $C_2$ - $C_7$  group,  $R^2$  is hydrogen or a methyl group,  $n$  is 0-2, and  $P$  represents a glycidyl ether group, a 3-halo-2-hydroxypropyl ether group, a 1,2-epoxy group, or a halide, and  
15

-one or more reagents C having the formula



wherein  $R^3$  represents a  $C_8$ - $C_{30}$  group,  $m$  is 0-10, and  $R^2$  and  $P$  have  
20 the meaning as described above.

2. A cellulose ether according to claim 1, characterized in that reagent A consists essentially of chloroacetic acid.
- 25 3. A cellulose ether according to claim 1 or 2, characterized in that  $P$  is a glycidyl ether group.
4. A cellulose ether according to any one of the preceding claims, characterized in that reagent B is butyl glycidyl ether.

5. A cellulose ether according to any one of the preceding claims, characterized in that  $R^3$  is a  $C_{12}$ - $C_{22}$  group.
- 5 6. A cellulose ether according to any one of the preceding claims, characterized in that reagent C is dodecyl glycidyl ether, tetradecyl glycidyl ether, hexadecyl glycidyl ether, octadecyl glycidyl ether, dodecyl-bis-oxyethyl glycidyl ether, tetradecyl-bis-oxyethyl glycidyl ether, hexadecyl-bis-oxyethyl glycidyl ether, octadecyl-bis-oxyethyl glycidyl ether, tetradecyl-penta-oxyethyl glycidyl ether, or a mixture thereof.
- 10 7. A cellulose ether according to any one of the preceding claims, characterized in that the alkali metal cellulose is reacted with reagents A, B, and C while gradually increasing the temperature.
- 15 8. A cellulose ether according to any one of preceding claims 1-6, characterized in that the alkali metal cellulose is reacted first with reagents B and C and then with reagent A.
- 20 9. A cellulose ether according to any one of preceding claims 1-6, characterized in that the alkali metal cellulose is reacted first with reagent A and then with reagents B and C.
- 25 10. A cellulose ether according to any one of the preceding claims, characterized in that the process is carried out using a minimal amount of a diluent.
11. A cellulose ether according to any one of the preceding claims, characterized in that the alkali metal cellulose is reacted with four



alkylating reagents A, B, C, and D, wherein A, B, and C have the meaning described in any one of the preceding claims, and D is a quaternary ammonium compound.

- 5 12. The use of a hydrophobically modified anionic cellulose ether according to any one of the preceding claims as a protective colloid, stabilizer, emulsifier, thickener, or rheology modifier.

# INTERNATIONAL SEARCH REPORT

Intr lonal Application No  
PCT/EP 98/03709

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08B11/193

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 362 769 A (AQUALON COMPANY) 11 April 1990 cited in the application see page 3, line 14 - line 40 ---	1-11
Y	US 2 463 869 A (ROBERT M. HAMILTON ET AL.) 8 March 1949 see column 1, line 20 - line 25 --- -/--	1-11

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

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Date of the actual completion of the international search

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# INTERNATIONAL SEARCH REPORT

International Application No

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	<p>PATENT ABSTRACTS OF JAPAN vol. 97, no. 8, 29 August 1997 &amp; JP 09 110901 A (KAO CORP), 28 April 1997 see abstract &amp; DATABASE WPI Week 9727 Derwent Publications Ltd., London, GB; AN 294981 see abstract</p> <p>---</p>	1-11
Y	<p>DE 554 877 C (I.G.FARBENINDUSTRIE) 15 July 1932 see page 1, line 35 - line 40</p> <p>---</p>	1-11
A	<p>EP 0 307 915 A (AQUALON COMPANY) 22 March 1989 cited in the application see claims 1-9</p> <p>-----</p>	

# INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No.

PCT/EP 98/03709

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 362769	A	11-04-1990	US 4904772 A	27-02-1990
			AT 120764 T	15-04-1995
			CA 1329590 A	17-05-1994
			DE 68922058 D	11-05-1995
			DE 68922058 T	28-09-1995
			JP 2169601 A	29-06-1990
US 2463869	A	08-03-1949	NONE	
DE 554877	C		NONE	
EP 307915	A	22-03-1989	US 4826970 A	02-05-1989
			AU 2233188 A	23-03-1989
			CA 1307258 A	08-09-1992
			CN 1032796 A,B	10-05-1989
			DE 3852739 D	23-02-1995
			DE 3852739 T	18-05-1995
			ES 2065904 T	01-03-1995
			FI 884281 A,B,	18-03-1989
			JP 1152102 A	14-06-1989
			JP 2647166 B	27-08-1997
			KR 9709895 B	19-06-1997
			NO 174057 C	09-03-1994